PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2004-253155
(43)Date of publication of application : 09.09.2004

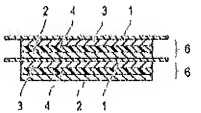
(51)Int.Cl. H01M 10/40
H01M 2/10
H01M 4/02
H01M 4/58
H01M 10/44
H01M 10/48

(21)Application number : 2003-039313
(22)Date of filing : 18.02.2003

(71)Applicant : NISSAN MOTOR CO LTD
(72)Inventor : FUKUZAWA TATSUHIRO
NEMOTO KOICHI

(54) BIPOLAR BATTERY

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a bipolar battery allowing its capacity to be adjusted by detecting a voltage of each cell layer in the battery without complicating the structure of the battery or impairing sealing capability of the battery.
SOLUTION: In relation to a bipolar lithium ion secondary battery composed by serially stacking, by interposing an electrolyte, a plurality of bipolar electrodes each having a positive electrode 2 formed on one surface of a collector 1, and a negative electrode 3 formed on the other surface thereof, a part of an electrode peripheral part of this bipolar battery is provided with a part where the collector is exposed without applying an insulation treatment.



CLAIMS

[Claim(s)]
[Claim 1]
In a bipolar rechargeable lithium-ion battery which laminated a bipolar electrode in which a cathode was formed in one field of a charge collector, and an anode was formed in a field of another side to two or more sheet series on both sides of an electrolyte,
A bipolar battery, wherein there is a portion which an insulation process was not made a part of electrode periphery, but a charge collector has exposed to it.
[Claim 2]
The bipolar battery according to claim 1, wherein voltage detection and a connector for capacity adjustments inserted in an inside from a battery exterior are connected to a charge collector exposed portion of said electrode periphery.
[Claim 3]
The bipolar battery according to claim 1 or 2 characterized by using carbon or a lithium transition metal multiple oxide as negative electrode active material using a lithium transition metal multiple oxide as positive active material.
[Claim 4]
A bipolar battery given in any 1 clause of Claims 1-3 using a solid polymer electrolyte for said electrolyte.
[Claim 5]
When voltage of each cell layer is individually detected via said voltage detection and connector for capacity adjustments and voltage of each cell layer reaches to predetermined charge final voltage at the time of charge, A control method of a bipolar battery given in any 1 clause of Claims 1-4 sending current through a current bypass circuit and arranging a charging state of each cell layer.
[Claim 6]
A cell group which connected and constituted the bipolar battery according to claim 1 to 4. [two or more]
[Claim 7]
Vehicles which carry a bipolar battery and/or the cell group according to claim 6 of a description in ********1**4 as a power supply for a drive, and are characterized by things.

[Translation done.]

* NOTICES *

1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to the bipolar battery with which it comes to arrange positive active material and negative electrode active material at the both sides of a charge collector.
[0002]
[Description of the Prior Art]
In recent years, reduction of carbon-dioxide emissions is eagerly desired for environmental protection. In the auto industry, expectations have gathered for reduction of the carbon-dioxide emissions by introduction of an electromobile (EV) and a hybrid electric vehicle (HEV), and development of the rechargeable battery for motor drives which holds the key to these utilization is performed wholeheartedly. Attentions have gathered for the rechargeable lithium-ion battery which can attain high energy density and high power density as a rechargeable battery. However, in order to apply to a car and to secure high power, it is necessary to connect in series and to use two or more rechargeable batteries.
[0003]
However, when a cell is connected via a terminal area, an output will decline with the electrical resistance of a terminal area. Also spatially, the cell which has a terminal area has a disadvantage. That is, the fall of the power density of a cell or an energy density is brought about by the terminal area.
[0004]
As what solves this problem, the bipolar battery using the bipolar electrode which has arranged positive active material and negative electrode active material on both sides of a charge collector is developed (for example, the patent documents 1, two references.).
[0005]
Among these, in the bipolar battery which uses a solid polymer electrolyte as an eleotrolyte, since a solution (electrolysis solution) is not included in a cell, there are no worries about liquid leakage or the generation of gas, and reliability is highly expected as what can provide the bipolar battery which does not need a sealing seal structurally. In the bipolar battery which uses a polymer gel electrolyte as an electrolyte, since it excels in ionic conductivity and the power density and the energy density of a cell are also fully obtained, it is expected as a bipolar battery nearest to a utilization stage.
[0006]
[Patent documents 1]
JP,2000-100471,A
[Patent documents 2]
JP,H11-204136,A
[0007]
[Problem to be solved by the invention]
However, since such a bipolar battery is laminated [the electrode] in series within the cell, when it has dispersion in capacity and internal resistance between each cell layer, there is a problem that the capacity (voltage) of cell layers varies, by repeating charge and discharge.
[0008]
By what the terminal 17 for voltage detection and capacity adjustments is taken out from each electrode to the exterior of the battery armor material 10, and is connected to the voltage detection and the current bypass circuit 41 which is an external control circuit (charging control circuit) as shown in drawing 8 (c) in order to solve the above-mentioned problem. The voltage of each cell layer 6 is detected individually, and performing capacity adjustment is also considered. The terminal 17 for voltage detection and capacity adjustments can consider what was extended until it extended some charge collectors 1 and exposed outside, as shown in drawing 8 (b) for example.
[0009]
However, in order to secure high power as EV or a power supply for HEV motor drives, it is necessary to increase the number of electrode laminations connected in series into a cell. Therefore, in the bipolar battery 11, the number of the terminals 17 for voltage detection and capacity adjustments for detecting voltage of each cell layer individually and carrying out capacity adjustment increases, for example, as for 30-40 layers (ten or more layers), the number of electrode laminations becomes ****** (a terminal -- ******) of a terminal, and becomes difficult [it / to take out only from a piece of a cell like drawing 8 (a)]. As a result, while structure of the terminal area circumference of the bipolar battery 11 becomes complicated, the new problem that a seal of a terminal ejection portion (refer to a portion enclosed with a circle among a figure.) becomes

sweet among seal part 10' of the battery armor material 10 circumferences (sealing nature falls) arises.
[0010]
Then, this invention is providing a bipolar battery which the target place's complicating structure's of a cell can also detect voltage of each cell layer in a cell, without spoiling the sealing nature of a cell, and can perform capacity adjustment, and a method for controlling the same.
[0011]
[Means for solving problem]
In a bipolar rechargeable lithium-ion battery with which this invention laminated a bipolar electrode in which a cathode was formed in one field of a charge collector, and an anode was formed in a field of another side to two or more sheet series on both sides of an electrolyte, A bipolar battery, wherein there is a portion which an insulation process was not made a part of electrode periphery, but a charge collector has exposed to it can attain.
[0012]
[Effect of the Invention]
In the bipolar battery of this invention, since there is a portion which an insulation process was not made a part of electrode periphery, but the charge collector has exposed to it, the connector for voltage detection and capacity adjustments is connectable with this portion from the exterior. Therefore, it is not necessary to take out the terminal for voltage detection and capacity adjustments from each electrode, and the structure of a cell does not complicate. It is not necessary to carry out the seal of the terminal for much voltage detection and capacity adjustments, and in order for what is necessary to be just to carry out the seal only of the connector for voltage detection and capacity adjustments taken out by the exterior of battery armor material, the sealing nature of a cell is not spoiled. By connecting the connector concerned, without that of an external control circuit, the voltage of each cell layer in a cell can be detected, and capacity adjustment of each cell layer, etc. can be performed. As a result, in various industries including power supplies for a drive, such as EV and HEV, it can become a useful power source.
[0013]
[Mode for carrying out the invention]
Hereafter, it explains about an embodiment of the invention.
[0014]
In the bipolar rechargeable lithium-ion battery with which the bipolar battery concerning this invention laminated the bipolar electrode in which the cathode was formed in one field of a charge collector, and the anode was formed in the field of another side to two or more sheet series on both sides of the electrolyte,
There is a portion which an insulation process was not made a part of electrode periphery, but the charge collector has exposed to it.
[0015]
First of all, the outline of the basic constitution of the bipolar battery of this invention is briefly explained using Drawings. Among these, the outline sectional view which expressed typically the structure of the bipolar electrode which constitutes a bipolar battery is shown in drawing 1, and to drawing 2. The outline sectional view which expressed typically the structure of the cell layer which constitutes a bipolar battery is shown, and to drawing 3. The outline sectional view which expressed the entire structure of the bipolar battery typically is shown, and the schematic view which meant notionally (symbolizing) coming in series to connect the cell layer by which plural laminates were carried out into the bipolar battery is shown in drawing 4.
[0016]
As shown in drawing 1 - 4, the electrode layers 2 and 3 of the ****** bipolar electrode 5 counter across the bipolar electrode 5 (refer to drawing 1) which formed the positive electrode layer 2 in one side of the charge collector 1 of one sheet, and formed the negative electrode layer 3 in another field, and the electrolyte layer 4. That is, it consists of the electrode layered product (main part of a bipolar battery) 7 of structure which laminated two or more bipolar electrodes (electrode layer) 5 which have the positive electrode layer 2 on a field of one of the two of the charge collector 1, and have the negative electrode layer 3 on a field of another side via the electrolyte layer 4 in the bipolar battery 11.
[0017]
The electrodes 5a and 5b of the top layer of the electrode layered product 7, and the bottom of the heap which laminated two or more sheets of such bipolar electrode 5 grade, It may not be bipolar electrode structure and is good also as a structure which has arranged an electrode layer (the positive electrode layer 2 or the negative electrode layer 3) of only one side required for the charge collector 1 (or tag block) (refer to drawing 3). In the bipolar battery 11, a cathode and the negative electrode leads (current terminal) 8 and 9 are joined to the charge collector 1 of top and bottom ends, respectively.
[0018]
Except for the part, an insulating part is formed in each electrode periphery of an insulation process in order to prevent a short circuit by irregular ** with a slight end of a laminated electrode from charge collector 1 comrades contacting, or an electrolysis solution beginning to leak from an electrolyte layer, or taking place. By the way, a characterizing portion of this invention is detailed to a part of each electrode periphery, and a point that an insulation process is not made is explained to it.
[0019]
The number of times of lamination of a bipolar electrode is adjusted according to voltage for which it asks. Even if it makes thickness of a sheet-shaped cell thin as much as possible, as long as sufficient output is securable, the number of times of lamination of a bipolar electrode may be lessened.
[0020]
In order to prevent a shock from the outside at the time of using it, and environmental degradation in the bipolar battery 11

of this invention, It is good to consider it as structure which carried out decompression enclosure of the electrode layered product 7 portion at the battery armor material (exterior package) 10, and took out the electrode leads 8 and 9 to the exterior of the battery armor material (exterior package) 10 (drawing 3, thing of four references). A wiring section of an external control circuit (for example, charging control circuit) connected to voltage detection and a connector for capacity adjustments, or this connector mentioned later also serves as structure taken out by the exterior of battery armor material (exterior package) (it explains in a place of a characterizing portion of this invention.). Aluminum from a viewpoint of a weight saving of a cell, stainless steel, nickel, Polymer-metal compound laminate films, such as an aluminum laminated pack which covered metal (an alloy is included), such as copper, with insulators, such as a polypropylene film, etc., Conventionally, using publicly known battery armor material, by joining a part or all of the periphery in thermal melting arrival, the electrode layered product 7 is stored, decompression enclosure (seal) is carried out, and they are the electrode leads 8 and 9 (further). It is preferred to have composition which took out a wiring section of voltage detection and a connector for capacity adjustments, or an external control circuit to the exterior of the battery armor material 10. The basic constitution of this bipolar battery 11 can say the cell layer (single cell) 6 which carried out plural laminates also with composition connected in series, as shown in drawing 4.

[0021]

The bipolar battery of this invention is used by movement of a lithium ion suitably for the bipolar rechargeable lithium-ion battery with which charge and discharge are carried. This has the high voltage of a cell compared with the usual rechargeable lithium-ion battery which is not a bipolar type, is because the cell excellent in output characteristics can be constituted, and is because high energy density and high power density can be attained as large capacity power supplies, such as an electromobile. however, if the effect of Hitoshi Kougami of a battery characteristic is acquired, it will not bar applying to the cell of other kinds.

[0022]

Next, it explains about the characterizing portion of this invention using Drawings. Drawing 5 is an outline top view of the bipolar battery which provides the portion which an insulation process was not made a part of electrode periphery, but the charge collector has exposed to it. Drawing 6 (a) is an outline perspective view of the side which enters in the cell of the voltage detection and the connector for capacity adjustments for inserting in an inside and connecting with the charge collector exposed portion of this electrode periphery from a battery exterior, Drawing 6 (b) is a near schematic view out of which it comes out of the cell of this voltage detection and connector for capacity adjustments, and drawing 6 (c) is an A-A line stairs section schematic view of drawing 6 (b). Drawing 7 is an outline perspective view of the cell showing the state where the connector of drawing 6 was connected to the charge collector exposed portion of the electrode periphery of drawing 5.

[0023]

In this invention, as drawing 1 - 4 explained, the positive electrode layer 2 is formed in one field of the charge collector 1, In the bipolar rechargeable lithium-ion battery 11 which laminated the bipolar electrode 5 in which the negative electrode layer 3 was formed in the field of another side to two or more sheet series across the electrolyte layer 4, As shown in drawing 5, there is the portion (it is also only called a charge collector exposed portion among this Description.) 23 which the insulating part 21 by an insulation process was not formed in a part of electrode periphery, but the charge collector 1 has exposed.

[0024]

With an electrode here, the electrode 5b which has arranged the negative electrode layer 3 may be included only in required one side of the bipolar electrode 5a and the charge collector 1 which have arranged the positive electrode layer 2 only on required one side of the charge collector 1 besides the bipolar electrode 5.

[0025]

The insulating part 21 in which the insulation process is made and formed except for a part of electrode periphery, Although what was formed in what is conventionally formed using a publicly known insulation process method, stuck insulating tape and films, such as a polyimide tape, for example, was formed, or each electrode periphery by pouring in and impregnating and immersing insulating resin etc. is mentioned, it is restricted to these and is not a thing.

[0026]

As for the above-mentioned charge collector exposed portion 23, it is desirable to provide in the same part of the periphery of each electrode so that voltage detection and the connector 31 for capacity adjustments can connect easily.

[0027]

The above-mentioned charge collector exposed portion 23 may be formed anywhere in an electrode periphery. Although drawing 5 (a) and drawing 7 showed the example provided in the neighborhood which counters the neighborhood by the side of extraction of a cathode and the negative electrode leads (current terminal) 8 and 9, It may provide the same neighborhood as the cathode [not the thing restricted to this in any way but] and negative electrode leads' (current terminal's) 8 and 9 extraction side, and may provide in the cathode and negative electrode lead (current terminal) 8, and long side side which adjoins the 9 extraction side. Preferably, providing in the position of drawing 5 (a) is desirable so that wiring of a battery exterior, etc. may not become complicated.

[0028]

What is necessary is just to determine width of the charge collector exposed portion 23 in consideration of a resistance reduction effect, the plug easy, etc. between connector weight increase and a connector by making capacity of a cell layer, and width large.

[0029]

In a bipolar battery of this invention, as shown in drawing 7, voltage detection and a connector for capacity adjustments (voltage detection and connector for capacity adjustments with a terminal connected with each electrode) inserted in an

inside from a battery exterior are connected to the charge collector exposed portion 23 of an electrode periphery. If this may provide a cell to which only voltage detection and a connector for capacity adjustments were connected according to the purpose of use or a using form (manufacture, sale), Also when it provides a cell by which voltage detection and a current bypass circuit (charging control circuit) which is an external control circuit were furthermore connected to voltage detection and a connector for capacity adjustments (manufacture, sale), it is for being certain. Since it is uneconomical to exchange the whole cell group when only one cell is faulty when using as a power supply of EV or a HEV motor for driving for example, with a form of a cell group etc. which are mentioned later, the former, When performing a changing battery individually, removing a poor cell from an external control circuit and exchanging for a new cell, it excels in a point that exchange cell expense can be held down. The latter is taking out a wiring section (for example, film wiring) which connected an external control circuit to voltage detection and the connector 31 for capacity adjustments from the battery armor material 10, Since the seal of the thick connector 31 is not carried out but what is necessary is just to carry out the seal of the wiring section of film state, it excels in a point that a cell which was more excellent in seal performance can be provided.

[0030]

In the cell 11 to which above-mentioned voltage detection and connector 31 for capacity adjustments were connected. By connecting the connector (not shown) provided in the wiring end part by the side of voltage detection and the current bypass circuit of each cell layer which is an external control circuit (charging control circuit), the voltage of each cell layer can be detected to the pin hole (or pin) 35 of the connector 31 concerned, and capacity adjustment of each cell layer, etc. can be performed to it. It is the same also by the cell to which the voltage detection and the connector 31 for capacity adjustments to which voltage detection and a current bypass circuit (charging control circuit) were beforehand attached as described above were connected.

[0031]

When connecting the voltage detection and the connector 31 for capacity adjustments by the side of a cell, and the connector (not shown) provided in the wiring end part by the side of voltage detection and a current bypass circuit (charging control circuit), it is good to make the voltage detection and the connector 31 for capacity adjustments by the side of a cell into a female die. This is the same Reason as usually making a power supply side into a female die. That is, it is because the danger of there being a possibility that pins may contact and leading to the short circuit of a cell, and also receiving an electric shock of a male when dealing with a cell by a charging state becomes high.

[0032]

As the voltage detection and a connector for capacity adjustments used for this invention, As shown in drawing 6, as a terminal connected with each electrode at the side which enters in a cell, So that the notch section 33 for inserting collector foil (charge collector exposed portion) may be formed and it can connect with the connector by the side of voltage detection and a current bypass circuit (charging control circuit) which is an external control circuit at the side which comes out of a cell, The pin hole (or pin) 35 is formed and that etc. to which each notching (terminal) part 33 and each pin hole 35 are electrically connected individually can be used. What is necessary is just to use insulating materials, such as insulating resin, for other connector bodies using high conductivity materials, such as copper, in the notch section 33, the pin hole (or pin) 35, or the terminal area 37 in the meantime. However, if the utilization objects (the simplification of the terminal for voltage detection, a sealing nature improved effect, etc.) as the voltage detection and a connector for capacity adjustments in this invention can be attained, it should not be restricted to what is illustrated above at all.

[0033]

The side which is not restricted and comes out of a cell should just be taken as the form where it united with the connector (commercial item) by the side of an external control circuit, especially concerning the form of voltage detection and the connector 31 for capacity adjustments. So that it can check that it has inserted in a right location, when also inserting in the charge collector exposed portion of each electrode besides form like drawing 6 (a) the side which enters in a cell, It will not be restricted especially if the purpose of this invention can attain that it may be the form which shifts each part which carries out a difference and can be arranged etc. Connecting a checking connector to voltage detection and the connector for capacity adjustments, and monitoring the open circuit voltage of a cell layer, the check of were able to insert in the right location of the charge collector exposed portion of each electrode may be inserted one by one, and it may be made to insert it at once.

[0034]

What is necessary is just to determine the interval of each insertion part of voltage detection and the connector for capacity adjustments in accordance with the electrode interlayer spacing of a corresponding cell.

[0035]

Next, as the control method of the bipolar battery concerning this invention, When the voltage of each cell layer in a cell is individually detected via voltage detection and the connector 31 for capacity adjustments and the voltage of each layer reaches to predetermined charge final voltage at the time of charge, Current is sent through the current bypass circuit (charging control circuit) which is an external control circuit, and the charging state of each cell layer is arranged. Thereby, the voltage of each cell layer can be detected and capacity adjustment of each cell layer, etc. can be performed. Therefore, since it can certainly charge at every charge to charge final voltage per all the cell layers when repeating charge and discharge even if dispersion in capacity and internal resistance is between each cell layer since the electrode is laminated in series within the cell, the charge voltages (capacity) of each cell layer can be arranged. Therefore, since this is always correctable using the external control circuit through the connector 31 in the case of the next charge even if dispersion arises for every cell layer at the time of discharge (uniformity), dispersion in the charging capacity of cell layers is always controllable to the minimum.

[0036]

Many cells are used in a power supply for motor drives etc. which consist of a cell group which made two or more (to in-series and/or parallel) connection of the bipolar battery 11 so that it might mention later and which will make two or more (to in-series and/or parallel) connection of this cell group if there is necessity further. Therefore, since a cell layer connected in series into this cell increases dramatically with the whole power supply, as for stopping capacity between these cell layers, and dispersion of internal resistance, difficulty and a yield also worsen. on the other hand . In a control method of this invention, a certain amount of dispersion of capacity between such cell layers or internal resistance can be permitted, and it can be said also as a very useful method.

[0037]

Although conventionally publicly known things, such as what combined a Zener diode voltage regulator and IC, are applicable to the above about voltage detection and a current bypass circuit which is an external control circuit of explanation, for example, it should not be restricted to these. When voltage of each cell layer is detected individually and voltage of each layer reaches like the above in this invention to predetermined charge final voltage (it is usually set as full charge voltage.) at the time of charge, What is necessary is just to attach voltage detection and a current bypass circuit which is an external control circuit set up send current through a current bypass circuit. Namely, what is necessary is to suspend charging current supply to the cell layer concerned, if it becomes predetermined charge voltages, to send current through an external current bypass circuit (capacitance adjusting circuit), and just to design an external control circuit not perform further charge (overcharge) of the cell layer concerned. Thereby, even if charging time of each cell layer has dispersion owing to dispersion, such as initial capacity, internal resistance, and after-discharge capacity (voltage), a charging state of each cell layer can be arranged. Therefore, it can suppress that dispersion in capacity (voltage) of cell layers increases gradually by repeating charge and discharge. As a result, reinforcement as the whole cell can be attained. When necessity was in voltage detection and a current bypass circuit which is an external control circuit further in this invention and voltage of each cell layer reaches cut-off voltage to specify also at the time of discharge, It cannot be overemphasized that it may control so that that current may be sent through a current bypass circuit and a control circuit etc. which can be prevented from carrying out overdischarge may be attached to it etc. can make a battery life last long more.

[0038]

As mentioned above, although explained focusing on a control method of detecting voltage of a cell via composition and this connector of a cell by which voltage detection and a connector for capacity adjustments were connected to a charge collector exposed portion and this charge collector exposed portion which are characterizing portions of this invention, and performing capacity adjustment, To especially other components of a bipolar battery of this invention, and a method for controlling the same, it should not be restricted and a thing of a publicly known bipolar battery can apply broadly conventionally.

[0039]

Although hereafter explained briefly for every component of a bipolar rechargeable lithium-ion battery of this invention, it cannot be overemphasized that this invention is not what should be restricted to these in any way.

[0040]

[A charge collector]

As a charge collector which can be used by this invention, Not a thing restricted especially but what is conventionally publicly known can be used, for example, aluminium foil, stainless steel foil, a clad plate of nickel and aluminum, a clad plate of copper and aluminum, or plating material of combination of these metal can be used preferably. It may be the charge collector which made a surface of metal cover aluminum. A charge collector which pasted two or more metallic foils together depending on the case may be used. It is preferred to use aluminium foil as a charge collector from viewpoints of corrosion resistance, the ease of making, economical efficiency, etc.

[0041]

Although thickness in particular of a charge collector is not limited, it is usually about 1-100 micrometers.

[0042]

[A positive electrode layer]

A positive electrode layer contains positive active material. In addition, lithium salt for improving a conductive auxiliary for improving electron conductivity, a binder, a polymer electrolyte, and ion conductivity, etc. may be contained.

[0043]

As positive active material, a multiple oxide (lithium transition metal multiple oxide) of a transition metal and lithium can be used conveniently. Specifically Li-Co system multiple oxides, such as $LiCoO_2$, What replaced some of Li-Fe system multiple oxides, such as Li-Mn system multiple oxides, such as Li-nickel system multiple oxides, such as $LiNiO_2$, and spinel $LiMn_2O_4$, and $LiFeO_2$, and these transition metals with other elements can be used. These lithium transition metal multiple oxide is excellent in reactivity and cycle durability, and is a low cost material. Therefore, by using such materials for an electrode, it is advantageous at a point which can form a cell excellent in output characteristics. In addition, a phosphoric acid compound and sulfated compound;V_2O_5 of transition metals, such as $LiFePO_4$, and lithium, Transition metal oxides and sulfides, such as MnO_2, TiS_2, MoS_2, and MoO_3 ;P bO_2, AgO, NiOOH, etc. are mentioned.

[0044]

The particle diameter of positive active material is good to use a thing smaller than the particle diameter generally used with a solution type lithium ion battery, in order to reduce the electrode resistance of a bipolar battery. Specifically, it is good in the mean particle diameter of positive-active-material particles being 0.1-5 micrometers.

[0045]

Acetylene black, carbon black, graphite, etc. are mentioned as the above-mentioned conductive auxiliary. However, it is not

necessarily restricted to these.
[0046]
Polyvinylidene fluoride (PVDF), SBR, polyimide, etc. can be used as the above-mentioned binder. However, it is not necessarily restricted to these.
[0047]
When using a solid polymer electrolyte for an electrolyte layer, it is desirable to contain the solid polymer electrolyte also in a positive electrode layer. By filling up the void between the positive active material in a positive electrode layer with a solid polymer electrolyte, it is because the ion conduction in a positive electrode layer becomes smooth and output improvement as the whole bipolar battery can be planned.
[0048]
On the other hand, when making a separator impregnate a polymer gel electrolyte and an electrolysis solution to an electrolyte layer and using them for it, the electrolyte does not need to be contained in the positive electrode layer and the conventionally publicly known binder which ties up positive-active-material particles should just be contained.
[0049]
Especially as a polymer for solid polymer electrolytes, it is not limited and polyethylene oxide (PEO), polypropylene oxide (PPO), these copolymers, etc. are mentioned. ** -- a polyalkylene oxide system polymer [like] may dissolve well lithium salt, such as $LiBF_4$, $LiPF_6$, $LiN(SO_2CF_3)_2$, and $LiN(SO_2C_2F_5)_2$. The outstanding mechanical strength is revealed by forming the structure of cross linkage. A solid polymer electrolyte is contained in either [at least] a positive active material layer or a negative electrode active material layer in this invention. However, in order to raise the battery characteristic of a bipolar battery more, being contained to both sides is preferred.
[0050]
As lithium salt, $LiBF_4$, $LiPF_6$, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, or these mixtures can be used. However, it is not necessarily restricted to these.
[0051]
Although a polymer gel electrolyte contains the electrolysis solution usually used for the solid polymer electrolyte which has ion conductivity with a lithium ion battery, the thing which made the same electrolysis solution hold is also further contained in the skeleton of a polymer without lithium ion conductivity.
[0052]
Here as an electrolysis solution (electrolyte salt and plasticizer) contained in a polymer gel electrolyte, What is necessary is to be used with a lithium ion battery and Usually, for example, $LiPF_6$, [just] $LiBF_4$, $LiClO_4$, $LiAsF_6$, Inorganic acid anionic salt, such as $LiTaF_6$, $LiAlCl_4$, and $Li_2B_{10}Cl_{10}$, $LiCF_3SO_3$, $Li(CF_3SO_2)_2N$, . Are chosen from organic acid anionic salt, such as Li $(C_2F_5SO_2)_2N$. Including at least one kind of lithium salt (electrolyte salt), propylene carbonate, Cyclic carbonate, such as ethylene carbonate; Dimethyl carbonate, Chain carbonate, such as methylethyl carbonate and diethyl carbonate; A tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1, 2-dimethoxyethane, ether [, such as 1,2-dibutoxyethane,]; -- lactone [, such as gamma-butyrolactone]; -- nitril [, such as acetonitrile]; -- ester species [, such as methyl propionate]; -- amide [, such as dimethylformamide]; -- methyl acetate. A thing using organic solvents (plasticizer), such as an aprotic solvent, etc. which mixed one kind or two sorts or more as being chosen from methyl formate as it is few can be used. However, it is not necessarily restricted to these.
[0053]
As a polymer without lithium ion conductivity used for a polymer gel electrolyte, polyvinylidene fluoride (PVDF), polyvinyl chloride (PVC), polyacrylonitrile (PAN), polymethylmethacrylate (PMMA), etc. can be used, for example. However, it is not necessarily restricted to these. Since it is a thing included in a category which does not rather almost have ion conductivity, it can also be considered as a polymer which has the above-mentioned ion conductivity, but PAN, PMMA, etc. are illustrated as a polymer without lithium ion conductivity used for a polymer gel electrolyte here.
[0054]
As the above-mentioned lithium salt, for example $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiTaF_6$, Organic acid anionic salt, such as inorganic acid anionic salt, such as $LiAlCl_4$ and $Li_2B_{10}Cl_{10}$, $Li(CF_3SO_2)_2N$, and $Li(C_2F_5SO_2)_2N$, or these mixtures can be used. However, it is not necessarily restricted to these.
[0055]
Although what is necessary is just to determine a ratio (mass ratio) of host polymer in a polymer gel electrolyte, and an electrolysis solution according to the purpose of use etc., ranges of it are 2:98-90:10. That is, also with an electrolysis solution from an outer peripheral part of an electrode layer oozing out, as drawing 8 explained, a seal can be effectively carried out by lengthening suitably an outer peripheral part of a gel electrolyte layer of this invention rather than an electrode end part. Therefore, priority should be comparatively given to a battery characteristic also about a ratio (mass ratio) of host polymer in the above-mentioned polymer gel electrolyte, and an electrolysis solution.
[0056]
Loadings of positive active material in a positive electrode layer, a conductive auxiliary, a binder, polymer electrolytes (host polymer, an electrolysis solution, etc.), and lithium salt should be determined in consideration of the purposes of using a cell (output serious consideration, energy serious consideration, etc.), and ion conductivity. For example, if there are too few loadings of a polymer electrolyte in a positive electrode layer, ion conduction resistance and ionic diffusion resistance within a positive electrode layer will become large, and battery capacity will fall. On the other hand, if there are too many loadings of a polymer electrolyte in a positive electrode layer, an energy density of a cell will fall. Therefore, in consideration of these

factors, the amount of polymer gel electrolytes corresponding to the purpose is determined.
[0057]
Thickness in particular of a positive electrode layer should not be limited, and as loadings were described, it should be determined in consideration of the purposes of using a cell (output serious consideration, energy serious consideration, etc.), and ion conductivity. Thickness of a general positive electrode layer is about 10-500 micrometers.
[0058]
[A negative electrode layer]
A negative electrode layer contains a negative-electrode-active-material active material. In addition, lithium salt for improving a conductive auxiliary for improving electron conductivity, a binder, polymer electrolytes (host polymer, an electrolysis solution, etc.), and ion conductivity, etc. may be contained.
[0059]
When using a solid polymer electrolyte for a high polymer electrolyte layer, it is desirable to contain a solid polymer electrolyte also in a negative electrode layer. By filling up a void between negative electrode active material in a negative electrode layer with a solid polymer electrolyte, it is because ion conduction in a negative electrode layer becomes smooth and output improvement as the whole bipolar battery can be planned.
[0060]
On the other hand, when using a polymer gel electrolyte for a high polymer electrolyte layer, a polymer electrolyte does not need to be contained in a negative electrode layer, and a conventionally publicly known binder which ties up negative-electrode-active-material particles should just be contained. Except a kind of negative electrode active material, since it is the same as that of contents fundamentally indicated by a clause of a "positive electrode layer", explanation is omitted here.
[0061]
As negative electrode active material, the negative electrode active material in which the lithium ion battery of a solution system is also used can be used. Although carbon, a metallic oxide, a lithium metal multiple oxide, etc. can be used, specifically, they are carbon or a lithium transition metal multiple oxide preferably. These carbon or a lithium transition metal multiple oxide is excellent in reactivity and cycle durability, and is a low cost material. Therefore, the cell excellent in output characteristics can be formed by using such materials for an electrode. As a lithium transition metal multiple oxide, lithium titanium multiple oxides, such as $Li_4Ti_5O_{12}$, etc. can be used, for example. As carbon, black lead, graphite, hard carbon, soft carbon, etc. can be used, for example.
[0062]
[Electrolyte layer]
Therefore, in this invention, it can apply also to the separator and ******** into which the (a) polymer gel electrolyte, the (b) solid polymer electrolyte, or the (c) electrolysis solution was infiltrated according to the purpose of use.
[0063]
(b) Polymer gel electrolyte
Especially as a polymer gel electrolyte, it should not be restricted and what is used for the conventional gel electrolyte layer can be used suitably. Here, the gel electrolyte refers to the thing which made the electrolysis solution hold in a polymer matrix. In this invention, the difference between all the solid polymer electrolytes (it is also only called a solid polymer electrolyte) and a gel electrolyte is as follows.
[0064]
- A thing having contained an electrolysis solution used for all the solid polymer electrolytes, such as polyethylene oxide (PEO), with the usual lithium ion battery is a gel electrolyte.
[0065]
- A thing which made an electrolysis solution hold in skeletons of a polymer without lithium ion conductivity, such as polyvinylidene fluoride (PVDF), also hits a gel electrolyte.
[0066]
- A ratio of constituting-gel electrolyte polymer (it is also called host polymer thru/or a polymer matrix.) and an electrolysis solution is broad, and in polymer 100 mass %, if all the solid polymer electrolyte and electrolysis solution 100 mass % is used as a liquid electrolyte, all the intermediate fields will hit a gel electrolyte.
[0067]
Although it should not be restricted and a publicly known thing can be conventionally used especially as host polymer of the above-mentioned gel electrolyte, Preferably Polyethylene oxide (PEO), polypropylene oxide (PPO), A polyethylene glycol (PEG), polyacrylonitrile (PAN), Poly vinylidene- fluoride hexafluoropropylene (PVdF-HFP), poly (methyl methacrylate) (PMMA), and those copolymers have them, and to a solvent. [desirable] Ethylene carbonate (EC), propylene carbonate (PC), gamma-butyrolactone (GBL), dimethyl carbonate (DMC), diethyl carbonate (DEC), and those mixtures are desirable.
[0068]
Especially as an electrolysis solution (electrolyte salt and plasticizer) of the above-mentioned gel electrolyte, it should not be restricted and a publicly known thing can be used conventionally. What is necessary is just specifically what is usually used with a lithium ion battery, For example, $LiPF_6$, $LiBF_4$, $LiClO_4$, $LiAsF_6$, $LiTaF_6$, $LiAlCl_4$, Inorganic acid anionic salt, such as $Li_2B_{10}Cl_{10}$, $LiCF_3SO_3$, . Are chosen from organic acid anionic salt, such as $Li(CF_3SO_2)_2N$ and $Li(C_2F_5SO_2)_2N$. Including at least one kind of lithium salt (electrolyte salt), propylene carbonate, Cyclic carbonate, such as ethylene carbonate; Dimethyl carbonate, Chain carbonate, such as methylethyl carbonate and diethyl carbonate; A tetrahydrofuran, 2-methyltetrahydrofuran, 1,4-dioxane, 1, 2-dimethoxyethane, ether [, such as 1,2-dibutoxyethane,]; -- lactone [, such as gamma-butyrolactone]; -- nitril [, such as acetonitrile]; -- ester species [, such as methyl propionate]; -- amide [, such as

dimethylformamide]; -- methyl acetate. . As being chosen from methyl formate, mixed one kind or two sorts or more as it is few. A thing using organic solvents (plasticizer), such as an aprotic solvent, etc. can be used. However, it is not necessarily restricted to these.

[0069]

If the electrolysis solution in the gel electrolyte in this invention carries out comparatively, it should not be restricted in particular, but it is desirable to consider it as number mass % - a 98 mass % grade from viewpoints of ionic conductivity etc. In especially this invention, it is effective about a gel electrolyte with many [the rate of an electrolysis solution] electrolysis solutions more than 70 mass %.

[0070]

In this invention, inside a gel electrolyte, it may be made for the quantity of the electrolysis solution contained in a gel electrolyte to become abbreviated homogeneity, and it may be lessened in inclination towards an outer peripheral part from the central part. The former is wide range, since it can obtain reactivity, it is preferred, and its latter is preferred at the point which can improve the sealing nature over the electrolysis solution of all the solid polymer electrolyte parts of an outer peripheral part. When lessening in inclination towards the outer peripheral part from the central part, it is desirable to use for the above-mentioned host polymer lithium ion conductivity existing polyethylene oxide (PEO), polypropylene oxide (PPO), and those copolymers.

[0071]

(b) Solid polymer electrolyte

Especially as all the solid polymer electrolytes, it should not be restricted and a publicly known thing can be used conventionally. It is a layer which specifically comprises a polymer which has ion conductivity, and material will not be limited if ion conductivity is shown. As all the solid polymer electrolytes, polyethylene oxide (PEO), polypropylene oxide (PPO), and a publicly known solid polymer electrolyte like these copolymers are mentioned. In a solid polymer electrolyte, in order to secure ion conductivity, lithium salt is contained. As lithium salt, $LiBF_4$, $LiPF_6$, $LiN(SO_2CF_3)_2$, $LiN(SO_2C_2F_5)_2$, or these mixtures can be used. However, it is not necessarily restricted to these. A polyalkylene oxide system polymer like PEOPPO may dissolve well lithium salt, such as $LiBF_4$, $LiPF_6$, $LiN(SO_2CF_3)_2$, and $LiN(SO_2C_2F_5)_2$. The outstanding mechanical strength is revealed by forming the structure of cross linkage.

[0072]

(c) A separator into which an electrolysis solution was infiltrated

Since the same thing as an electrolysis solution (electrolyte salt and plasticizer) contained in an already explained polymer gel electrolyte of a positive electrode layer can be used as an electrolysis solution into which a separator can be infiltrated, explanation here is omitted.

[0073]

Especially as the above-mentioned separator, it should not be restricted, a publicly known thing can be used conventionally, and porous sheets (for example, polyolefin system fine porous separator etc.) which consist of polymer which carries out absorption maintenance of the above-mentioned electrolysis solution can be used. The above-mentioned polyolefin system fine porous separator which has chemically the character to be stable, to an organic solvent has the outstanding effect that reactivity with an electrolyte (electrolysis solution) can be stopped low.

[0074]

As construction material of this polymer, polyethylene (PE), polypropylene (PP), a layered product that has a three-tiered structure of PP/PE/PP, polyimide, etc. are mentioned, for example.

[0075]

Although it cannot specify uniquely from changing with usage as thickness of the above-mentioned separator, in a use of rechargeable batteries for motor drives, such as an electromobile (EV) and a hybrid electric vehicle (HEV), etc., it is desirable that it is 4-60 micrometers in a monolayer or a multilayer. it generates, when a particle eats into a separator because thickness of a separator is in this range -- simplistic -- since it says that it is desirable prevention and to narrow inter-electrode for high power, there is an effect of a mechanical strength of a thickness direction and reservation of high power nature. When connecting two or more cells, since an electrode area increases, in order to improve the reliability of a cell, it is desirable to use a separator of a thick form also in a mentioned range.

[0076]

As for a path of micropore of the above-mentioned separator, it is desirable that it is 1 micrometer or less (it is usually about tens of nm in an aperture) at the maximum. Since it says that a "shutdown phenomenon" which a separator carries out melting with heat because a pitch diameter of micropore of a separator is in a mentioned range, and micropore closes occurs promptly, reliability goes up at the time of abnormalities, and it is effective in heat resistance improving as the result. When battery temperature rises by a surcharge (at the time of abnormalities), it becomes impossible to pass along Li ion by a "shutdown phenomenon" in which a separator carries out melting and which micropore closes occurring promptly in the anode (-) side from a cathode (+) of a cell (electrode), and it becomes impossible that is, to charge more. Therefore, it becomes impossible to overcharge and a surcharge is solved. As a result, the heat resistance (safety) of a cell improves, and also a heat sealed part (seal part) of battery armor material can be prevented from gas coming out and opening. A pitch diameter of micropore of a separator observes a separator with a scanning electron microscope etc., and is computed here as a pitch diameter which processed the photograph statistically with an image analyzer etc.

[0077]

As for a void content of the above-mentioned separator, it is desirable that it is 20 to 50%. it is because a particle pierces [prevention of loss of power by electrolytic (electrolysis solution) resistance, and] through a hole (micropore) of a separator

because a void content of a separator is in a mentioned range -- simplistic -- since it is called prevention, it is effective in securing both an output and reliability. A void content of a separator is a value calculated as a volume ratio from density of raw-material resin, and density of a separator of a final product here.

[0078]

The amount of impregnation of an electrolysis solution to the above-mentioned separator may be made to impregnate exceeding the liquid retaining ability range concerned although what is necessary is just to make it impregnate to a liquid retaining ability range of a separator. Since resin is poured into an electrolyte seal part, an electrolysis solution from an electrolyte layer oozes and ** can be prevented, this can be impregnated if it is a range which can carry out liquid retaining to this electrolyte layer. When this electrolysis solution pours resin into an electrolyte seal part, it leaves a dipping mouth (every one place each; a charge collector exposed portion before connector insertion may be used) for every inter-electrode one, After pouring in by the vacuum pouring-in method etc. from here, a separator can be made to impregnate an electrolysis solution by conventionally publicly known methods -- resin is injected into the dipping mouth concerned and a seal can be thoroughly carried out to it.

[0079]

An electrolyte layer of above-mentioned (1) - (3) may be used together in one cell.

[0080]

Although a polymer electrolyte may be contained in a polymer gel electrolyte layer, a positive active material layer, and a negative electrode active material layer, the same polymer electrolyte may be used for it and a polymer electrolyte which changes with layers may be used for it.

[0081]

By the way, host polymer for polymer gel electrolytes used preferably now is a polyether system polymer like PEO and PPO. For this reason, oxidation resistance by the side of a cathode under high temperature service is weak. Therefore, when using a cathode agent with a high oxidation-reduction potential generally used with a lithium ion battery of a solution system, few things are more preferred than capacity of a cathode in which capacity of an anode counters via a polymer gel electrolyte layer. Cathode potential can be prevented from going up too much at a charging end term if less than capacity of a cathode in which capacity of an anode counters. Capacity of a cathode and an anode can be calculated from manufacturing conditions as theoretical capacity at the time of manufacturing a cathode and an anode. Capacity of finished goods may be measured directly with a measuring device.

[0082]

However, since there is a possibility that anode potential may fall too much and the endurance of a cell may be spoiled when small compared with the capacity of the cathode which counters the capacity of an anode, it needs to be cautious of charge and discharge voltage. For example, it is set as a suitable value to the oxidation-reduction potential of the positive active material which uses the average charge voltages of the cell (cell layer) of 1, and warns against endurance falling.

[0083]

The thickness in particular of the electrolyte layer which constitutes a cell is not limited. However, in order to obtain a compact bipolar battery, it is preferred to make it thin as much as possible in the range which can secure the function as an electrolyte. 5-200 micrometers of thickness of a general electrolyte layer are about 10-100 micrometers preferably.

[0084]

[Insulating part (portion in which the insulation process is made)]

An insulating part is the purpose of preventing the short circuit by irregular ** with a slight end of a laminated electrode from charge collectors contacting, or an electrolysis solution beginning to leak, or taking place, and it comes to form it in the circumference (periphery) of each electrode. However, in this invention, as shown in drawing 5 (a), it has a charge collector exposed portion by which the insulation process is not made at a part of electrode periphery. Since this charge collector exposed portion was already explained as a characterizing portion of this invention, explanation here is omitted.

[0085]

Although what is necessary is to have insulation, sealing nature (sealing performance) over a break through of an electrolysis solution or moisture permeation of moisture from the outside, the heat resistance under battery operation temperature, etc., and just to be able to use an epoxy resin, rubber, polyethylene, polypropylene, polyimide, etc. as an insulating part, From viewpoints of corrosion resistance, chemical resistance, the ease (film production nature) of making, economical efficiency, etc., an epoxy resin is preferred. An insulating part should not be restricted [form / especially / after / pour in, immerse and / applying such a material, dry hardening may be carried out, it may be formed, and / insulating tape or films, such as a polyimide tape, / stick and].

[0086]

[A cathode and a negative pole terminal board]

What is necessary is just to use a cathode and a negative pole terminal board if needed. When using, it has a function as a terminal, and also the thinner one as much as possible is good from a viewpoint of slimming down, but as for each of electrodes and electrolyte layers which it comes to laminate, and charge collectors, since the mechanical strength is weak, it is desirable to give only intensity which carries out ****** support of these from both sides. Thickness of a cathode and a negative pole terminal board can be said for about 0.1-2 mm to be usually desirable from a viewpoint of stopping internal resistance in a terminal area.

[0087]

Construction material usually used with a lithium ion battery can be used for construction material of a cathode and a negative pole terminal board. For example, aluminum, copper, titanium, nickel, stainless steel (SUS), these alloys, etc. can be used. It is preferred to use aluminum from viewpoints of corrosion resistance, the ease of making, economical efficiency, etc.

[0088]
The same construction material may be used for the construction material of a positive pole terminal board and a negative pole terminal board, and the thing of different construction material may be used for it. These cathodes and a negative pole terminal board may laminate to a multilayer that from which construction material differs.
[0089]
A cathode and the negative pole terminal board should just be the same sizes as a charge collector.
[0090]
[A cathode and a negative electrode lead (current terminal)]
About a cathode and a negative electrode lead, the publicly known lead used with the usual lithium ion battery can be used.
[0091]
[Battery armor material (cell case)]
A bipolar battery is good to accommodate the whole cell layered product which is a main part of a bipolar battery in battery armor material thru/or a cell case (not shown), in order to prevent the shock from the outside at the time of using it in order to prevent the shock from the outside, and environmental degradation, and environmental degradation. A polymer-metal compound laminate film, an aluminum laminated pack, etc. which covered metal (an alloy is included), such as aluminum, stainless steel, nickel, and copper, with insulators, such as a polypropylene film, from a viewpoint of a weight saving, It is preferred by joining a part or all of the periphery in thermal melting arrival using publicly known battery armor material conventionally to have composition which stored and sealed the cell layered product. In this case, the above-mentioned cathode and a negative electrode lead should just be taken as the structure which is inserted into the above-mentioned heat sealed part, and is exposed to the exterior of the above-mentioned battery armor material. It is preferred to use the polymer-metal compound laminate film excellent in thermal conductivity, an aluminum laminated pack, etc. at the point that heat can be efficiently told from the heat source of a car, and the inside of a cell can be quickly heated to battery operation temperature.
[0092]
Next, it can be considered as the cell group which connected and constituted the above-mentioned bipolar battery from this invention. [two or more] That is, high capacity and a high-output battery module can be formed by connecting in series and/or in parallel, and constituting and cell-group-izing the bipolar battery of this invention using at least two or more pieces. Therefore, it becomes possible to satisfy comparatively inexpensive the demand to the cell capacity and the output for every purpose of use.
[0093]
Concrete for example, the above-mentioned bipolar battery is connected to N piece parallel, and the bipolar battery made N piece parallel is made into M more piece series, and it stores to the battery case made of metal thru/or resin, and is considered as a cell group. Under the present circumstances, the series / the number of multiple connection of a bipolar battery are determined according to the purpose of use. For example, what is necessary is just to combine so that it can apply to the power supply for a drive of the vehicles with which high energy density and high power density are called for as large capacity power supplies, such as an electromobile (EV) and a hybrid electric vehicle (HEV). What is necessary is just to electrically connect the positive pole terminal for cell groups and a negative pole terminal, and the electrode lead of each bipolar battery using a lead etc. What is necessary is just to electrically connect using a suitable connecting member like a spacer or a bus bar, when connecting bipolar batteries in series/in parallel. However, the cell group of this invention should not be restricted to what was explained here, and a publicly known thing can be conventionally used for it suitably.
[0094]
In this invention, it can be considered as the vehicles which carry an above-mentioned bipolar battery and/or cell group as a power supply for a drive. The bipolar battery and/or cell group of this invention have the various characteristics as mentioned above, and are an especially compact cell. For this reason, about an energy density and power density, it is suitable as power supplies for a drive, such as the vehicles with which an especially severe demand is made, for example, an electromobile, and a hybrid electric vehicle, and an electromobile and a hybrid car excellent in fuel consumption and traveling performance can be provided. For example, since carrying a cell group as a power supply for a drive under the seat of the body center section of an electromobile thru/or the hybrid electric vehicle can take in-company space and a large trunk room, it is convenient. However, in this invention, not the thing that should be restricted to these in any way but a cell group thru/or a cell can be installed in the under floor of vehicles, a trunk room, an engine room, a roof, and a bonnet hood etc. It may be made to carry a bipolar battery not only depending on a cell group but depending on usage, and may be made to carry in this invention combining these cell groups and a bipolar battery. Although an above-mentioned electromobile and hybrid electric vehicle are preferred as vehicles which can carry the bipolar battery and/or cell group of this invention as a power supply for a drive, it is not restricted to these.
[0095]
Especially as a manufacturing method of a bipolar battery of this invention, it should not be restricted and various kinds of publicly known methods can be used suitably conventionally. Below, it explains briefly.
[0096]
(1) Spreading of a constituent for cathodes
First, a suitable charge collector is prepared. A constituent for cathodes is usually obtained as a slurry (slurry for cathodes), and is applied to one field of a charge collector.
[0097]
A slurry for cathodes is a solution containing positive active material. As other ingredients, a conductive auxiliary, a binder, a polymerization initiator, electrolytic raw materials (a polymer for solid electrolytes thru/or host polymer, an electrolysis

solution, etc.), a supporting electrolyte (lithium salt), a slurry viscosity adjustment solvent, etc. are arbitrary, and are contained. That is, the slurry for cathodes can mix and produce material which is arbitrary and contains a conductive auxiliary, an electrolytic raw material, a supporting electrolyte (lithium salt), a slurry viscosity adjustment solvent, a polymerization initiator, etc. besides negative electrode active material like a lithium ion battery of a solution system by a predetermined ratio.

[0098]

When using a polymer gel electrolyte for an electrolyte layer, a conductive auxiliary for improving conventionally a publicly known binder which ties up positive-active-material particles, and electron conductivity, a solvent, etc. should just be contained, and host polymer, an electrolysis solution, lithium salt of a raw material of a polymer gel electrolyte, etc. do not need to be contained. It is also the same as when using a separator which made an electrolyte layer impregnate an electrolysis solution.

[0099]

As for an electrolytic polymer raw material (host polymer of a raw material of a polymer gel electrolyte thru/or polymer raw material of a solid polymer electrolyte), it is preferred for PEO, PPO(s), these copolymers, etc. to be mentioned and to have the functional groups (carbon-carbon double bond etc.) of cross-linking in intramolecular. A mechanical strength improves by constructing a bridge in a polymer electrolyte using a functional group of this cross-linking.

[0100]

A compound mentioned above can be used about positive active material, a conductive auxiliary, a binder, lithium salt, and an electrolysis solution.

[0101]

It is necessary to choose a polymerization initiator according to a compound to polymerize. For example, azobisisobutyronitrile is mentioned as benzyl dimethyl ketal and a thermal polymerization initiator as a photopolymerization initiator.

[0102]

Slurry viscosity adjustment solvents, such as NMP, are chosen according to a kind of slurry for cathodes.

[0103]

What is necessary is just to adjust an addition of positive active material, lithium salt, a conductive auxiliary, and a binder according to the purpose of a bipolar battery, etc., and it should just add quantity usually used. An addition of a polymerization initiator is determined according to the number of cross-linking functional groups contained in an electrolytic polymer raw material. Usually, it is a 0.01 - 1 mass % grade to a polymer raw material.

[0104]

(2) Formation of a positive electrode layer (electrode formation part)

A charge collector in which a slurry for cathodes was applied is dried, and a solvent contained is removed. Crosslinking reaction is advanced depending on a slurry for cathodes, and, simultaneously with it, a mechanical strength of a solid polymer electrolyte may be raised. The desiccation can use a vacuum dryer etc. Although conditions of desiccation are determined according to an applied slurry for cathodes and it cannot specify uniquely, they are usually 5 minutes - 20 hours at 40-150 **. By this drying process, a positive electrode layer (electrode formation part) is formed on a charge collector.

[0105]

(3) Spreading of a constituent for anodes

A constituent for anodes (slurry for anodes) containing negative electrode active material is applied to a field where a positive electrode layer was applied, and a field of an opposite hand.

[0106]

A slurry for anodes is a solution containing negative electrode active material. As other ingredients, a conductive auxiliary, a binder, a polymerization initiator, (a polymer for solid electrolytes thru/or host polymer, an electrolysis solution), etc., supporting electrolytes (lithium salt), a slurry viscosity adjustment solvent, etc. are arbitrary, and are contained. About a raw material and an addition which are used, since it is the same as that of explanation by a clause of "spreading of a constituent for (1) cathodes", explanation is omitted here.

[0107]

(4) Formation of a negative electrode layer (electrode formation part)

A charge collector in which a slurry for anodes was applied is dried, and a solvent contained is removed. Crosslinking reaction is advanced depending on a slurry for anodes, and, simultaneously with it, a mechanical strength of a polymer gel electrolyte may be raised. A bipolar electrode is completed according to this work. The desiccation can use a vacuum dryer etc. Although conditions of desiccation are determined according to an applied slurry for anodes and it cannot specify uniquely, they are usually 5 minutes - 20 hours at 40-150 **. By this drying process, a negative electrode layer (electrode formation part) is formed on a charge collector.

[0108]

(5) Formation of an electrolyte layer

When using a polymer solid electrolyte layer, it is manufactured by stiffening a solution which was made to dissolve a high-cost-of-raw-materials molecule of a solid polymer electrolyte, lithium salt, etc. in a solvent like NMP, and was prepared, for example. When using a polymer gel electrolyte layer, it is manufactured by, for example, polymerizing simultaneously with stoving a pregel solution which consists of host polymer, an electrolysis solution and lithium salt, a polymerization initiator, etc. under an inert atmosphere as a raw material of a polymer gel electrolyte (crosslinking reaction is promoted).

[0109]

applying the prepared above-mentioned solution or a pregel solution for example, on the above-mentioned electrode (a

cathode and/or anode) -- an electrolyte layer of predetermined thickness -- or -- the -- a part (electrolyte membrane about the half of electrolyte layer thickness) is formed. Then, by polymerizing an electrode by which an electrolyte layer (film) was laminated simultaneously with hardening or stoving (crosslinking reaction is promoted), an electrolytic mechanical strength is raised and film production formation of the electrolyte layer (film) is carried out (it is made to complete).

[0110]

Or an electrolyte layer laminated by inter-electrode or its part (electrolyte membrane about the half of electrolyte layer thickness) is prepared separately. An electrolyte layer (film) applies the above-mentioned solution or a pregel solution on suitable films, such as a PET film, and is manufactured by making it polymerize simultaneously with hardening or stoving (crosslinking reaction is promoted).

[0111]

Hardening or the stoving can use a vacuum dryer (vacuum oven) etc. Although conditions of stoving are determined according to a solution or a pregel solution and it cannot specify uniquely, it is usually 0.5 to 12 hours at 30-110 **.

[0112]

Thickness of an electrolyte layer (film) is controllable using a spacer etc. When using a photopolymerization initiator, it is good to slush into a gap of a light transmittance state, to irradiate with ultraviolet rays using a black light which can perform desiccation and photopolymerization, to carry out photopolymerization of the polymer in an electrolyte layer, to advance crosslinking reaction, and to produce a film. However, of course, it is not limited to this method. According to a kind of polymerization initiator, radiation initiated polymerization, an electron beam polymerization, thermal polymerization, etc. are used properly.

[0113]

Since a film used above may be heated by about 80 ** by a manufacturing process, it has sufficient heat resistance about [concerned] temperature, and there is no reactivity with a solution or a pregel solution further, Although it exfoliates and removes by a manufacturing process, and also [required] it is desirable to use a thing excellent in a mold-release characteristic, for example, it can use polyethylene terephthalate (PET), a polypropylene film, etc., it should not be restricted to these.

[0114]

Width of an electrolyte layer is made a little smaller than charge collector size of a bipolar electrode in many cases.

[0115]

About a composition component of the above-mentioned solution or a pregel solution, or its loadings, it should be suitably determined according to the purpose of use.

[0116]

A separator into which an electrolysis solution was infiltrated, It is the same composition as an electrolyte layer used for a bipolar battery of the conventional solution system which is not a bipolar type, Since it can manufacture conventionally with various publicly known manufacturing methods, for example, a method, the vacuum pouring-in method, etc. which put between a bipolar electrode a separator into which an electrolysis solution was infiltrated, and laminate it, detailed explanation is omitted hereafter.

[0117]

(7) Lamination with a bipolar electrode and an electrolyte layer

**1. After carrying out stoving enough under a high vacuum, in the case of a bipolar electrode in which an electrolyte layer (film) was formed in the whole surface or both sides, two or more electrodes in which an electrolyte layer (film) was formed are started in suitable size, a started electrode is pasted together directly, and a main part of a bipolar battery (electrode layered product) is produced in it.

[0118]

2. When a bipolar electrode and an electrolyte layer (film) are produced independently, after carrying out stoving enough under a high vacuum, two or more each is started for a bipolar electrode and an electrolyte layer (film) in suitable size. Predetermined number ******** and a main part of a bipolar battery (electrode layered product) are produced for a bipolar electrode and an electrolyte layer (film) which were started.

[0119]

The number of laminations of the above-mentioned electrode layered product is determined in consideration of the battery characteristic for which a bipolar battery is asked. In the outermost layer by the side of a cathode, the electrode in which only the positive electrode layer was formed on the charge collector is arranged. In the outermost layer by the side of an anode, the electrode in which only the negative electrode layer was formed on the charge collector is arranged. As for the stage of making the electrode which laminated the bipolar electrode and the electrolyte layer (film) or in which the electrolyte layer (film) was formed laminating, and obtaining a bipolar battery, it is preferred to perform from a viewpoint to prevent that moisture etc. mix in the inside of a cell under an inert atmosphere. For example, it is good to produce a bipolar battery under argon atmosphere and a nitrogen atmosphere.

[0120]

(8) Formation of an insulating part

At this invention, it is 1. The neighborhood of the outer peripheral part of the above-mentioned electrode layered product may be made immersed into an epoxy resin (precursor solution) by predetermined width from the outside neighborhood, an epoxy resin may be stiffened after that, an insulating part may be formed, and it is 2. That insulating tape or films, such as a polyimide tape, may be stuck for the neighborhood of the periphery of the bipolar electrode obtained above (4), and an insulating part may be formed etc. also about the method of an insulating part, and also a formation stage, It can be said that what is necessary is just to carry out not at the thing which should be restricted especially but at a formation stage suitable

for a formation method. Anyway, what is necessary is to mask a part of electrode periphery suitably, or to provide the portion which does not stick a tape in it, and just to form the portion which an insulation process was not carried out but the charge collector has exposed in this invention. It cannot be overemphasized that not the thing restricted to these but conventionally publicly known insulation process technology can be suitably used in this invention.

[0121]

(9) Attachment of voltage detection and the connector for capacity adjustments

In this invention, voltage detection and the connector 31 (the case where the external control circuit is further connected to this connector is included) for capacity adjustments are inserted and attached to the charge collector exposed portion of an electrode periphery.

[0122]

As a method (manufacture procedure) of inserting a connector in the charge collector exposed portion of each electrode, For example, after laminating an electrode and an electrolyte, inserting the notch section 33 of the connector 31 in charge collector 1 foil (portion used as a charge collector exposed portion) (if there is necessity further) After masking a connector part, may perform an insulation process to an electrode periphery, may form the insulating part 21, and, May laminate an electrode and an electrolyte, inserting the notch section 33 of the connector 31 in the charge collector exposed portion of charge collector 1 foil with which the insulation process was carried out except for a part of electrode periphery, and connecting with it, and, It should not be restricted [insert / in the charge collector exposed portion of an electrode layered product / the connector 31] in particular.

[0123]

(10) Packing (completion of a cell)

Finally, a positive pole terminal board and a negative pole terminal board are installed, respectively on both the outermost layers of the main part of a bipolar battery (cell layered product), and a positive electrode lead and a negative electrode lead are further joined and (it electrically connects) taken out to this positive pole terminal board and a negative pole terminal board. Although it should not be restricted especially as a joining method of a positive electrode lead and a negative electrode lead, and ultrasonic welding with low welding temperature, etc. can use suitably, it should not be limited to this and a publicly known joining method can be used suitably conventionally.

[0124]

The whole cell layered product is closed with battery armor material thru/or a cell case, in order to prevent a shock from the outside, and environmental degradation, and a bipolar battery is completed. In this case, a positive electrode lead, a negative electrode lead, and a connector (or that wiring section) are closed, and that part is taken out to a battery exterior (refer to drawing 7). Metal (aluminum, stainless steel, nickel, copper, etc.) with which an inner surface was covered by insulators, such as a polypropylene film, is preferred for construction material of battery armor material (cell case).

[0125]

[Working example]

An effect of this invention is explained using the following working example and comparative examples. However, technical scope of this invention is not limited to the following working example.

[0126]

Working example 1

<Manufacture of a cell>

1. Formation of positive electrode layer

As positive active material, as spinel $LiMn_2O_4$ [41.7 Mass %] with a mean particle diameter of 2 micrometers and a conductive auxiliary as host polymer of a raw material of acetylene black [8.3 mass %] and a polymer electrolyte, As a copolymer (a copolymerization ratio used 5:1 and weight average molecular weight used a thing of 8000.) [33.3 Mass %] of polyethylene oxide (PEO) and polypropylene oxide (PPO), and a supporting electrolyte (lithium salt), It is N-methyl-2-pyrrolidone (NMP) (NMP) as $Li(C_2F_5SO_2)_2N$ [16.7 Mass %] and a slurry viscosity adjustment solvent. Since it is made to volatilize altogether at the time of electrode desiccation and removes, it is not a component of an electrode, Optimum dose was added so that it might become suitable slurry viscosity. And as a thermal polymerization initiator. Material which consists of azobisuisobutironitoriru (they are 1000 mass ppm to the amount of host polymer) was mixed by the above-mentioned ratio (a ratio converted of an ingredient except a slurry viscosity adjustment solvent and a thermal polymerization initiator is shown.), and a cathode slurry was produced.

[0127]

Applied the above-mentioned cathode slurry to one side of the SUS foil (20 micrometers in thickness) which is a charge collector, put into vacuum oven, it was made to harden by thermal polymerization simultaneously [with desiccation] for 10 minutes at 120 **, and the positive electrode layer with a dry thickness of 50 micrometers was formed.

[0128]

2. Formation of negative electrode layer

As negative electrode active material, as $Li_4Ti_5O_{12}$ [21.8 Mass %] and a conductive auxiliary as acetylene black [8.4 mass %] and host polymer of the raw material of a polymer electrolyte, As the copolymer (the copolymerization ratio used 5:1 and weight average molecular weight used the thing of 8000.) [42.1 Mass %] of polyethylene oxide (PEO) and polypropylene oxide (PPO), and a supporting electrolyte (lithium salt), It is NMP (NMP) as $Li(C_2F_5SO_2)_2N$ [21.3 Mass %] and a slurry viscosity adjustment solvent. Since it is made to volatilize altogether at the time of electrode desiccation and removes, it is not a component of an electrode, Optimum dose was added so that it might become suitable slurry viscosity. And as a thermal polymerization initiator. The material which consists of azobisuisobutironitoriru (they are 1000 mass ppm to the amount of

host polymer) was mixed by the above-mentioned ratio (the ratio converted of the ingredient except a slurry viscosity adjustment solvent and a thermal polymerization initiator is shown.), and the anode slurry was produced. The mean particle diameter of the aggregated particle of $Li_4Ti_5O_{12}$ used for negative electrode active material had become the structure which is 10 micrometers and a 0.2-0.5-micrometer primary particle necked to some extent.

[0129]

The above-mentioned anode slurry was applied, it put into vacuum oven, the opposite side of the SUS foil in which the positive electrode layer was formed was stiffened by thermal polymerization simultaneously [with desiccation] for 10 minutes at 120 **, and the negative electrode layer with a dry thickness of 50 micrometers was formed in it.

[0130]

The bipolar electrode was formed by forming a positive electrode layer and a negative electrode layer in both sides of the SUS foil which is a charge collector, respectively.

[0131]

3. Formation of insulating part

The polyimide tape was stuck on the circumference of the bipolar electrode, and the insulating part was formed. A tape was not stuck on the part (the center section of the piece of an electrode; refer to [drawing 5 (a)]), but the charge collector was exposed to it.

[0132]

4. Formation of polymer electrolyte (layer) film

The 50-micrometer-thick electrolyte membrane was laminated to the cathode of the bipolar electrode which formed the cathode and the anode in both sides, respectively, an anode, and each field.

[0133]

Production of polymer electrolyte membrane was performed as follows. $LiN(SO_2C_2F_5)_2$ as 53 mass % and lithium salt for the following polymer raw material 26 mass %, After preparing benzyl dimethyl ketal as a photopolymerization initiator and preparing the **** solution for dry acetonitrile as 0.1 mass [of a polymer raw material] %, in addition a solvent, acetonitrile was removed by vacuum distillation. Thickness was specified using the Teflon (registered trademark) spacer, the high solution of this viscosity was filled on the positive electrode layer of the bipolar electrode which formed the positive electrode layer and the negative electrode layer in both sides, respectively, it irradiated with ultraviolet rays for 20 minutes, and photopolymerization (bridge construction) was carried out. The film was taken out, it put into the vacuum housing, stoving was carried out under a 12-hour high vacuum at 90 **, and the 50-micrometer-thick electrolyte membrane was formed except for residual water and a solvent. Similarly, the above-mentioned viscous high solution was filled also on [of the bipolar electrode] the negative electrode layer, it irradiated with ultraviolet rays for 20 minutes, and photopolymerization (bridge construction) was carried out. The film was taken out, it put into the vacuum housing, stoving was carried out under a 12-hour high vacuum at 90 **, and the 50-micrometer-thick electrolyte membrane was formed except for residual water and a solvent.

[0134]

The network polymer raw material of a polyether form compounded in accordance with the method of document (J. Electrochem. Soc., 145 1521(1998).) was used for the polymer raw material.

[0135]

5. Formation of bipolar battery

The bipolar electrode in which the electrolyte membrane was formed was laminated so that a cathode and an anode might counter on both sides of an electrolyte, and the cell layer was formed.

[0136]

The electrode was laminated and it was considered as the cell layered product so that five-layer (part for cell layer 5 cell) formation of the cell layer might be carried out.

[0137]

The connector for voltage detection was connected to the charge collector exposed part of this cell layered product after electrode lamination (refer to drawing 7). The whole was closed by the laminated pack so that the terminal of the connector for voltage detection might be exposed out of a cell, and the bipolar battery was constituted. The electrode lead (current terminal) was taken out from the battery armor material of the neighborhood which counters outside the connector's for voltage detection extraction side, as shown in drawing 7.

[0138]

The comparative example 1

Stick a polyimide tape on the whole circumference of a bipolar electrode, form an insulating part, and a charge collector exposed part is not provided. And except not having attached a connector for voltage detection, a cell layered product which carried out five-layer (part for cell layer 5 cell) lamination like working example 1 was closed by a laminated pack (what laminated aluminum with a polypropylene film; battery armor material), and a bipolar battery was formed. An electrode lead (current terminal) was taken out from battery armor material outside.

[0139]

<Evaluation>

A charge-and-discharge cycle test was done about a cell which connected to a connector for voltage detection of a bipolar battery of working example 1 a capacitance adjusting circuit (charging control circuit) which bypasses current when a cell reached full charge voltage, and a bipolar battery without a connector for voltage detection and a capacitance adjusting circuit of the comparative example 1. A bipolar battery of the comparative example 1 had the capacity of each cell layer after

20 cycles as smallest as the largest thing, and 18% of difference had produced it. Capacity variation of each cell layer of a bipolar battery of working example 1 was settled to less than 3% to it.

[Brief Description of the Drawings]

[Drawing 1]It is the section schematic view which expressed typically the basic structure of the bipolar electrode which constitutes the bipolar battery of this invention.

[Drawing 2]It is the section schematic view which expressed typically the basic structure of the cell layer (single cell) which constitutes the bipolar battery of this invention.

[Drawing 3]It is the section schematic view which expressed the basic structure of the bipolar battery of this invention typically.

[Drawing 4]It is a schematic view which expresses the basic constitution of the bipolar battery of this invention typically.

[Drawing 5]It is an outline top view of the bipolar battery which provides the portion which an insulation process was not made a part of electrode periphery, but the charge collector has exposed to it.

[Drawing 6]Drawing 6 (a) is an outline perspective view of the side which enters in the cell of the voltage detection and the connector for capacity adjustments for inserting in an inside and connecting with the charge collector exposed portion of this electrode periphery from a battery exterior.

Drawing 6 (b) is a near schematic view out of which it comes out of the cell of this voltage detection and connector for capacity adjustments, and drawing 6 (c) is an A–A line stairs section schematic view of drawing 6 (b).

[Drawing 7]Drawing 7 is an outline perspective view of the cell showing the state where the connector of drawing 6 was connected to the charge collector exposed portion of the electrode periphery of drawing 5.

[Drawing 8]Drawing 8 (a) is an outline top view of the cell at the time of taking out the terminal for voltage detection and capacity adjustments from each electrode to the exterior of battery armor material. Drawing 8 (b) is an outline top view showing the example extended until it extended some charge collectors 1 and exposed outside as a terminal for voltage detection and capacity adjustments of drawing 8 (a). Drawing 8 (c) is an approximate account figure showing the cell showing the state where took out the terminal for voltage detection and capacity adjustments from each electrode to the exterior of battery armor material, and it connected with the voltage detection and the current bypass circuit which is an external control circuit (charging control circuit).

[Explanations of letters or numerals]

1 -- Charge collector (metallic foil),
2 -- Positive electrode layer,
3 -- Negative electrode layer,
4 -- Electrolyte layer (electrolyte membrane),
5 -- Bipolar electrode
5a -- Electrode which has arranged the positive electrode layer only on required one side of a charge collector,
5b -- Electrode which has arranged the negative electrode layer only on required one side of a charge collector,
6 -- Cell layer (single cell),
7 -- Electrode layered product,
8 -- Positive electrode lead (current terminal),
9 -- Negative electrode lead (current terminal),
10 -- Battery armor material,
10' -- Seal part of the circumference of battery armor material,
11 -- Bipolar battery
17 -- Terminal for voltage detection and capacity adjustments,
21 -- Insulating part,
23 -- Charge collector exposed portion without an insulating part,
31 -- Voltage detection and connector for capacity adjustments,
33 -- Notch section
35 -- Pin hole
37 -- Terminal area in a connector,
41 -- Voltage detection and current bypass circuit.

[Translation done.]